

Likelihood of Forming Copper-Enamel Separating Surface Through Roasting

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Abstract

The article deals with the ascertaining the likelihood of the formation of separating surface in the process of enamel surface roasting. The assumption made is based on the evaluation of copper-enamel roasting thermodynamic process. Cohesion of these materials with B-O-Cu, Al-O-Cu, Ba-O-Cu bonds and the II group elements of the periodic system is the result of copper metallide creation.

Keywords: Enamel, Copper, Separating surface, Silicide, Thermodynamic measurement

Introduction

In the copper enameling process the reason of merging two different materials is the formation of oxygen bridges [1,2] between enamel and copper while roasting. The following schematic recording is applicable to visualize the process:

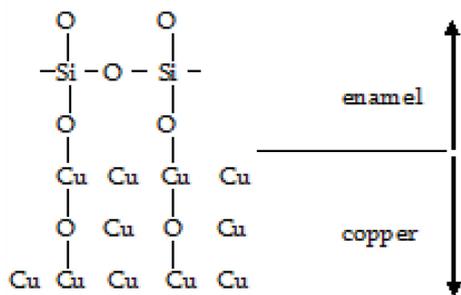


Figure 1. Bridge bonding between copper and enamel according to Ditsel.

As noted in the references, there is a likelihood of forming extended middle (transitional) layer on both sides of separating surface. However, bridge bonding creation is considered as the preferable option.

Creation of oxygen bridges implies oxidation of surface and surficial copper atoms that is thermodynamically possible [3]. Oxidation is proved by the fact that in neutral or reduction area enamel melt causes no copper wetting.

Not neglecting creation of copper oxides (mainly Cu₂O), we believe that the conception on enamel and copper oxygen bonding fails to completely resolve merging reason of these materials. This doubt is caused by the fact that it is hard to assume joint "sharing" of copper oxide oxygen with silicon or one of the silicon oxygen with copper.

Here we can bring two justifications. One is related to the data proved by the experiments that in Cu₂-CuO-SiO₂ system creation of silicates is impossible [4]. The fact of oxygen bridge creation between Cu and Si contradicts to enamel micro heterogeneity structure, whereas polar and non-polar structural units are merged. Two options of oxygen bridge

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creation exist in the above structure. According to the first option, copper atoms displace alkali, or alkali earth ion from polar grouping, or replace silicon atoms in non-polar grouping. Implementation of both options is practically impossible.

Based on the above discussion, the assumption is made that the cause of copper and enamel merging results due to various reasons. We believe that the cohesion between these materials is the result of separator development.

Methodology

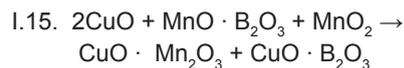
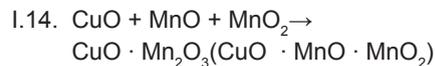
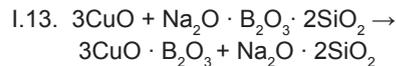
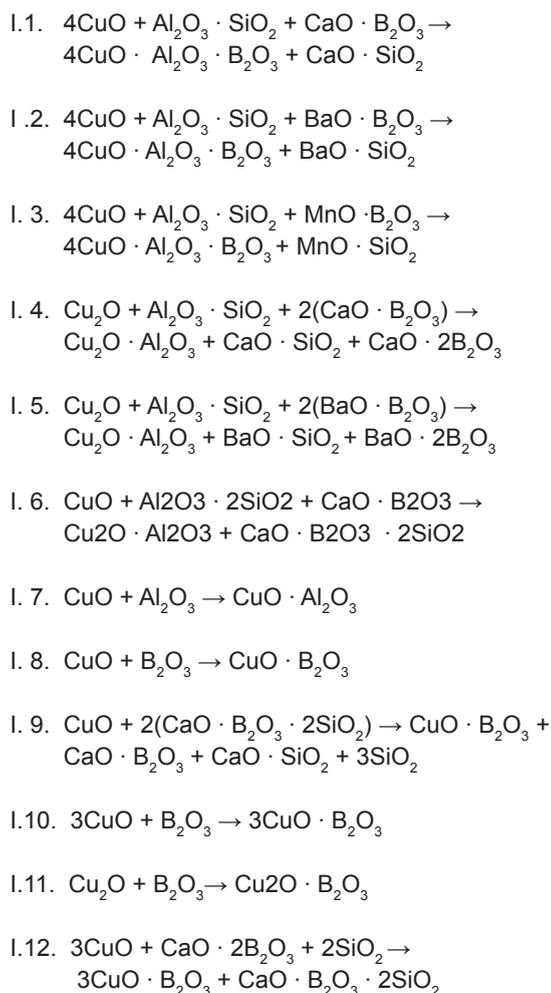
For verifying our assumption the Gibbs energy minimization method was applied using Ulich first approximation - the calculation is made on the assumption that the specific heat of the reaction components is unknown.

Thermodynamic assessment of the possible interactions between the copper and enamel structural units were carried out at the surface roasting temperature.

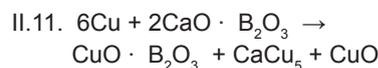
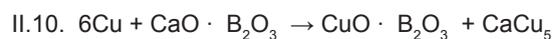
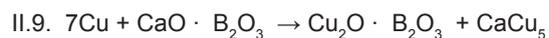
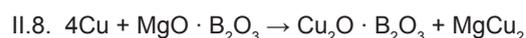
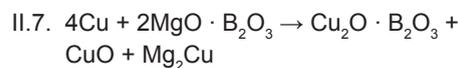
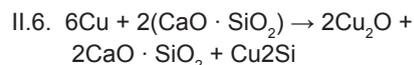
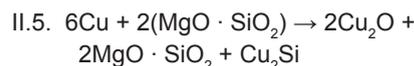
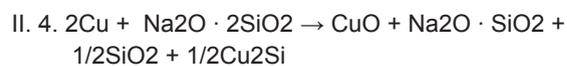
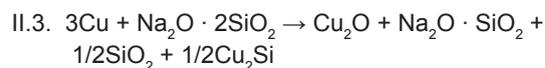
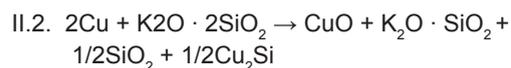
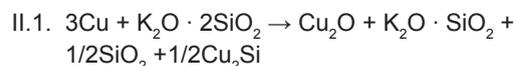
Results

More than a hundred reactions occurred during the experiments. Part of them is presented below.

1. Reactions with silicates, borate, aluminate and manganite creation:



2. Reactions resulting in formation of copper silicide and metallide:



While developing the interactions, it was observed that practically every copper compound is thermodynamically undefined. To determine their $\Delta H_{f,298}^0$ and S_{298}^0 , we applied the authors' proposed method [5]. The results are given in Table 1.

The first Group reaction thermodynamic assessment results are given in Table 2.

Table 3 presents $\Delta G_{T,R}^0$ and $\lg K_p$ quantities at roasting temperature.

The results of thermodynamic measurements of the reactions, given in the tables above, prove that the majority of interactions are energetically profitable with the exception of reactions 5 and 11. Although thermodynamic measurement provides a less kinetic side, the possibility of reactions is clearly reflected.

Definition of $\lg K$ gave us additional information. It was

Table 1. Thermodynamic characteristics of compounds

Mixture	$-\Delta H_{f,298}^{\circ}$ kcal/mol	S_{298}° cal/K·mol
$Cu_2O \cdot Al_2O_3$	455,37	39,56
$CuO \cdot Mn_2O_3$	265,50	39,05
$CuO \cdot Al_2O_3$	439,92	24,13
$4CuO \cdot Al_2O_3 \cdot B_2O_3$	909,07	76,00
$3CuO \cdot Al_2O_3$	530,12	50,17
$BaO \cdot 2B_2O_3$	778,20	32,13
$2MgO \cdot B_2O_3$	643,27	27,13
$MnO \cdot B_2O_3$	427,34	30,87
$MgO \cdot B_2O_3$	483,17	21,62
$2CaO \cdot B_2O_3$	653,79	34,66
$2MnO \cdot B_2O_3$	532,88	45,71
$3CaO \cdot B_2O_3$	820,11	43,90
$3MgO \cdot B_2O_3$	801,24	33,36
$3MnO \cdot B_2O_3$	636,17	59,75
$Na_2O \cdot B_2O_3 \cdot 2SiO_2$	909,68	50,1
$Cu_2O \cdot B_2O_3$	397,55	39,44
$3CuO \cdot B_2O_3$	465,40	46,05

Table 2. Results of thermodynamic assessment of the reactions

№	Thermodynamic measurement results		
	$\Delta H_{f,298,R}^{\circ}$ kcal/mol	$S_{298,R}^{\circ}$ cal/K·mol	$\Delta G_{T,R}^{\circ} = f(T)$ kcal/mol
I.1	-57,38	6,79	-57,38-0,0068 T
I.2	-51,56	5,83	-51,56-0,0058 T
I.3	-40,15	2,68	-40,15-0,0027 T
I.4	-19,49	-4,02	-19,49+0,0040 T
I.5	15,36	-6,54	15,36+0,0065 T
I.6	-55,90	11,63	-55,90-0,0116 T
I.7	-4,84	1,77	-4,84-0,0018 T
I.8	-40,15	2,74	-40,15-0,0027 T
I.9	-17,87	16,3	-17,87-0,0163 T
I.10	-57,4	2,58	-57,4-0,0026 T
I.11	4,28	-14,34	4,28+0,0143 T
I.12	-51,04	1,28	-51,04-0,0013 T
I.13	-32,48	4,78	-32,48-0,0048 T
I.14	-14,54	1,91	-14,54-0,0019 T
I.15	-23,62	0,95	-23,62-0,0010 T

Table 3. Thermodynamic characteristics of the reactions at 1123K

№	$\Delta G_{T,R}^{\circ}$ kcal/mol	$\lg K_p$
I. 1	-65,01	12,65
I. 2	-58,07	11,31
I. 3	-43,18	8,40
I. 4	-15,00	2,92
I. 5	22,66	- 4,42
I. 6	-68,93	13,41
I. 7	-6,86	1,33
I.8	-43,18	8,40
I. 9	-36,17	7,04
I. 10	-60,32	11,74
I. 11	20,34	-3,96
I. 12	-52,50	10,22
I. 13	-37,87	7,37
I. 14	-16,67	3,24
I. 15	-24,74	4,81

Table 4. Thermodynamic characteristics of the reactions

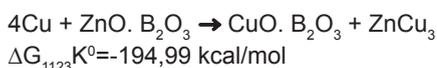
№	$\Delta G_{1123,R}^{\circ}$ kcal/mol	$\Delta G_T^{\circ} = f(T)$ kcal/mol
II. 1	42,03	43,94-0,0017 T
II. 2	43,72	46,64-0,0026 T
II. 3	42,43	42,32-0,0001 T
II. 4.	49,76	44,93+0,0043·T
II. 5.	75,07	83,47+0,0075·T
II 6	84,14	93,66+0,0085·T
II.7	186,96	201,45-0,029·T
II.8	- 45,66	-35,31-0,0092·T
II.9	64,24	76,26-0,0107·T
II.10	- 20,31	8,10-0,0253·T
II.11	113,55	118,94-0,0048·T

proved that two (4 and 14) of the above reactions are reversible at 1123 K; one (the 7th) is close to equilibrium, but the others have to be fully completed.

Thermodynamic results of II group reactions are given in Table 4.

The data given in the above tables indicate the tendencies characterizing II group reactions. The majority of the interactions with metallide creation are thermodynamically unprofitable. The exceptions are those reactions which result in obtaining CaCu, ZnCu, ZnCu₃, Cd₃Cu, BaCu₃.

The reaction is given as an example:



Conclusion

Based on the experimental data it was defined that:

1. Creation of Si-O-Cu bonding in the copper-enamel interaction is less possible thermodynamically; If we emphasize bridge bonding, there is a higher possibility of forming B-O-Cu, Al-O-Cu, Ba-O-Cu bondings;

2. Thermodynamic declines silicide creation on the separator surface, confirming the possibility of copper metallide creation for R²⁺ II group elements of periodic system.

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